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Nanomagnetics

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14. ABSTRACT
A simple and versatile chemical method is used to open tips of multiwall carbon nanotubes (MWCNTs) and fill with magnetic material. The process so far has succeeded in opening up the tips of all MWCNTs observed, but only few of the tubes were filled. The process is being fine tuned to fill a significant number of the MWCNTs with the sought compound. In this report, we will present the transmission electron microscope, energy dispersive spectroscopy, and Mössbauer spectroscopy studies on the filled MWCNTs.

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1. Introduction

Since the first comprehensive and detailed characterization in 1991 (*1*), the saga to impregnate multiwall carbon nanotubes (MWCNTs) with different types of application-related materials has continued (*2–14*). Nanomagnets are important as vital components in nano-electromechanical systems (NEMS) and have potential applications ranging from medicine, to defense, and to the way we explore the fabrics of our universe. The list of applications of CNTs filled with magnetic material can be extended to include materials for wearable electronics (*15*), cantilever tips in magnetic force microscopes (*16*), magnetic stirrers in microfluidic devices, and magnetic valves in nanofluidic devices (*17*). Biomedical applications include capsules or nanosubmarines for magnetically guided drug delivery to desired locations in the body, and nonpervasive diagnosis and treatment that can bypass surgery. Nanomagnets are also important from a fundamental point of view in understanding the physics of one-dimensional (1-D) magnets. Nanomagnets are likely to replace today's unstructured magnetic media in the near future. Magnetic storage density has made dramatic progress from ~1 Mbit/in^2 to 50 Gbit/in^2 in the last 20 years. Today's magnetic media consist of many tiny polycrystalline grains with a random distribution of magnetization directions. At present, magnetic media are initially unstructured, the position and shape of data bits are determined by the writing process. Signal-to-noise considerations demand that there be at least 1000 polycrystalline grains per bit. Increasing the storage density cannot be achieved by reducing the number of grains per bit, but a reduction of the size of individual grains would be necessary. However, as the grain size decreases, thermal fluctuation will randomly flip the magnetization. This thermal instability is called "superparamagnetism" and is believed to present a fundamental limit for today's magnetic storage paradigm. The use of patterned magnetic media and magnetic nanostructures offers the possibility to increase magnetic storage density by a factor of around 100 beyond the superparamagnetic limit. A particularly attractive option is to store each bit in an individual single-domain magnetic nanostructure, as opposed to a conglomerate of ~1000 as is done today. A single domain magnetic structure can be synthesized inside a CNT.

It is well known that CNTs are filled by foreign materials through capillarity mechanism. Capillarity is a two-step phenomenon: first, the liquid material wets the surface of the tube, then the material will be sucked by the open-end tube. Capillarity action depends on surface tension of the liquid material. Low surface tension materials, less than ~200 mN/m, wet the surface. Wetting is necessary for capillarity to occur, as can be seen from the Laplace equation,

$$\Delta P = \frac{2\gamma\cos\theta}{r}, \tag{1}$$

where r is the radius of curvature, ΔP is the pressure difference across the liquid-vapor interface, γ is the surface tension, and θ is the liquid-solid contact angle. The contact angle is related to the interfacial tensions. Wetting and hence capillary filling occurs when the liquid-solid contact angle θ_c<90o. θ_c is related to the liquid surface tension γ by

$$\text{Cos}\ \theta_c = (\gamma_{SV} - \gamma_{SL})\ \gamma^{-1}\ , \tag{2}$$

where γ_{SV} and γ_{SL} are the surface tensions at the solid-vapor and solid-liquid interfaces, respectively.

2. Experiment

The primary aims of the project was to synthesize a permanent magnetic alloy using wet chemistry inside MWCNTs, to characterize by transmission electron microscope (TEM), and to also further characterize the magnetic material in the inside of the MWCNTs by Mössbauer spectroscopy. The MWCNTs used are research grade from Nano-lab, Inc. (www.nano-lab.com) (95% pure, 20–50 nm in diameter, and 5–20 µm in length). The following procedure was followed to fill MWCNTs with $Sm_2Fe_{17}N_x$:

1. Suspend 0.20-g MWCNTs (20–50 nm in diameter and 5–20 µm long on the average) in 20-g nitric acid (HNO_3) containing 0.8 g of hydrated iron nitrate ($Fe(NO_3)_39H_2O$), which is ~5% w/w and 0.1 g of hydrated samarium nitrate ($Sm(NO_3)_36H_2O$).
   - MWCNTs were supplied by Nano-lab, Inc. (www.nano-lab.com) (lot 020806LP).
   - Nonahydrated iron nitrate ($Fe(NO_3)_39H_2O$), 99.99% pure, was supplied by the Alfa Aesar company (www.alfa.com).
   - Hexahydrated samarium nitrate ($Sm(NO_3)_36H_2O$), 99.9% purity, was supplied by the Alfa Aesar company (www.alfa.com, item no. 11224).
2. Reflux for 4.5 hr in a silicon oil bath at 100 ^oC under a stream of nitrogen.
3. Allow the suspension to settle for 16 hr and decant the supernatant solution.
4. Dry the resulting black insoluble product at RT under vacuum condition.

Figure 1 depicts the setup for the reflux procedure. After measured amounts of nitric acid, iron nitrate, samarium nitrate, and MWCNTs were mixed in the flask shown as black due to the color of the CNTs. The flask was lowered into a boiling silicon oil at 100 ^oC.

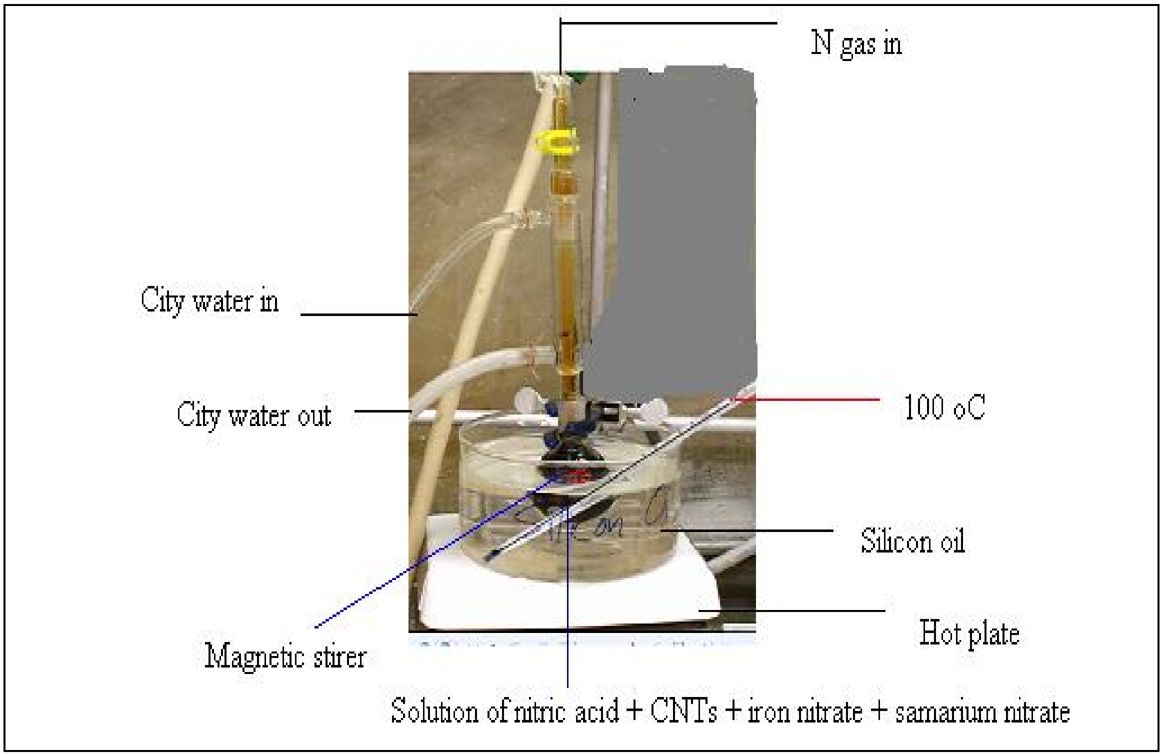

Figure 1. Refluxing in hot oil bath.

3. Results

Samples of filled MWCNTs were suspended in dimethylformamide for TEM analysis. As shown in figure 2, the refluxing process in nitric acid has opened the tips of 100% of the observed MWCNTs. This has been first shown by the work of the Oxford group (*2*). The reflux process breaks the carbon bond at the tips, not at the sides of CNTs. The tips are closed by caps that are curved, composed of a polygonal or cone shaped structure, usually a polygon C_5 which is highly reactive compared to the sides, which are composed of hexagonal network structure sp^2 –bonded carbon.

Figure 3 shows a network of MWCNTs filled with magnetic matter taken at 300 kV accelerating potential and at 100,000 magnification. A limited number of filling occurred, as shown in the figure. The darker spots in the figure were analyzed with the energy dispersive spectroscope (EDS) attached to the TEM and all were found to be iron particles of length ranging from 5 to 30 nm. Although this result is tantalizing, the yield of partially filled nanotubes has been small, the encapsulate being a minor product alongside empty nanotubes.

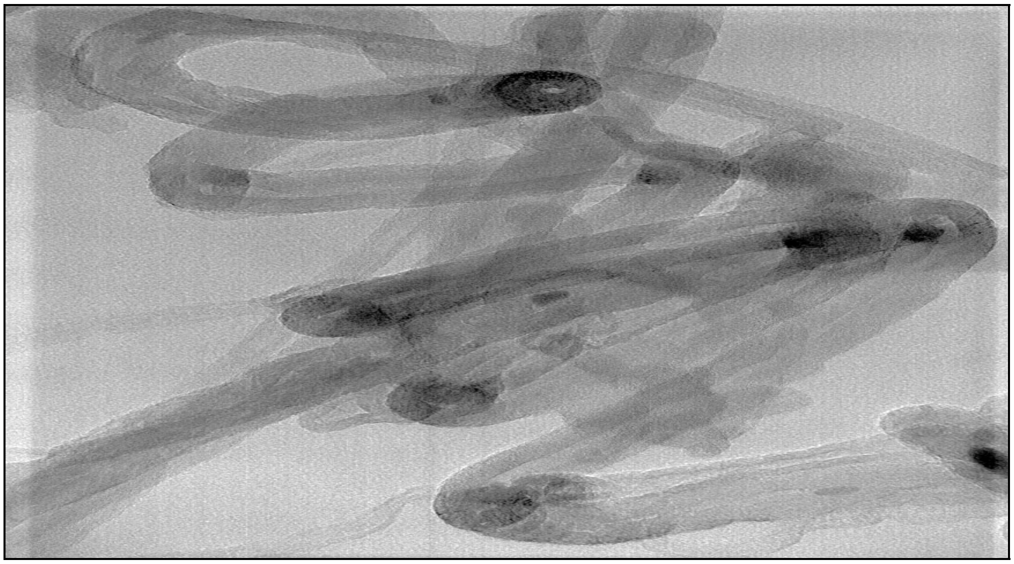

Figure 2. Tips of MWCNTs.

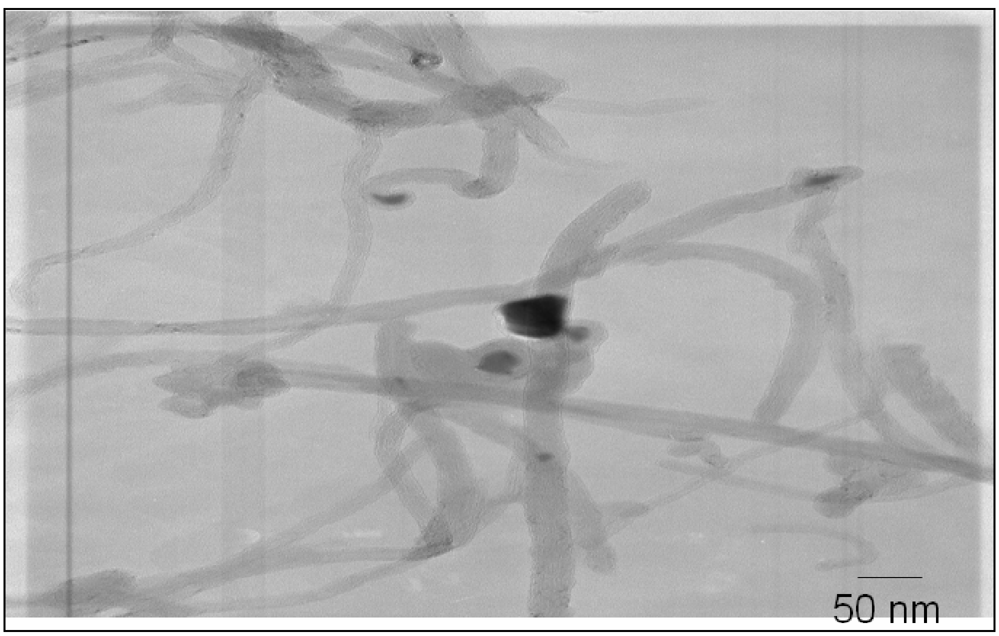

Figure 3. TEM of a network of open ended MWNTS with some filling of Fe.

Figure 4 shows a typical filled MWCNT at 10^6 magnification. The length of the filling which shows up as a region of darker contrast in the image is 28 nm, with a diameter of 9 nm. An EDS graph of the filled MWCNT shown in figure 4 is presented in figure 5. In the EDS, there is a carbon peak because of the MWCNT, a copper peak because of the TEM grid, and an iron peak because of the filling inside the MWCNT shown in the figure 5.

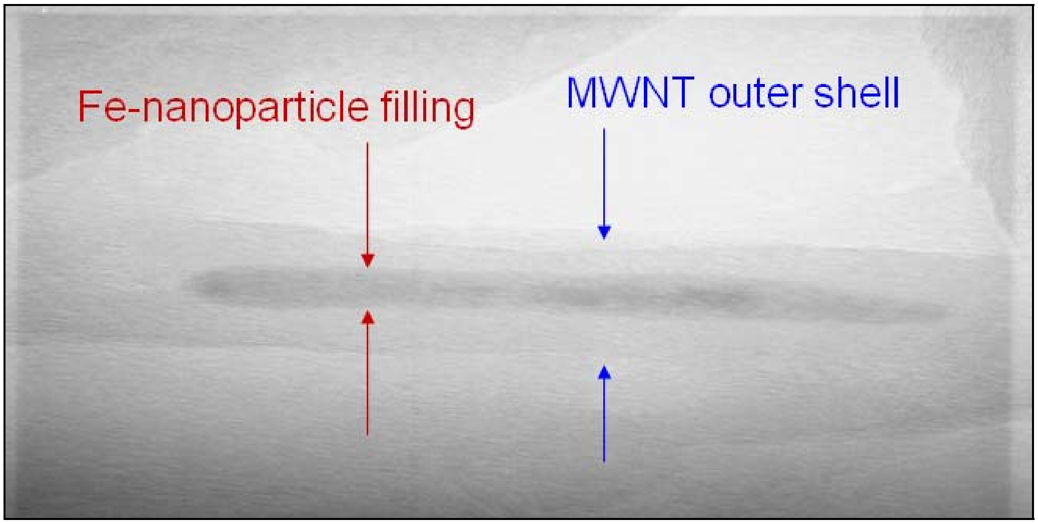

Figure 4. A single MWNT showing a significant filling with an outer diameter of ~30 nm and an inner diameter of ~10 nm filled with Fe nanoparticles.

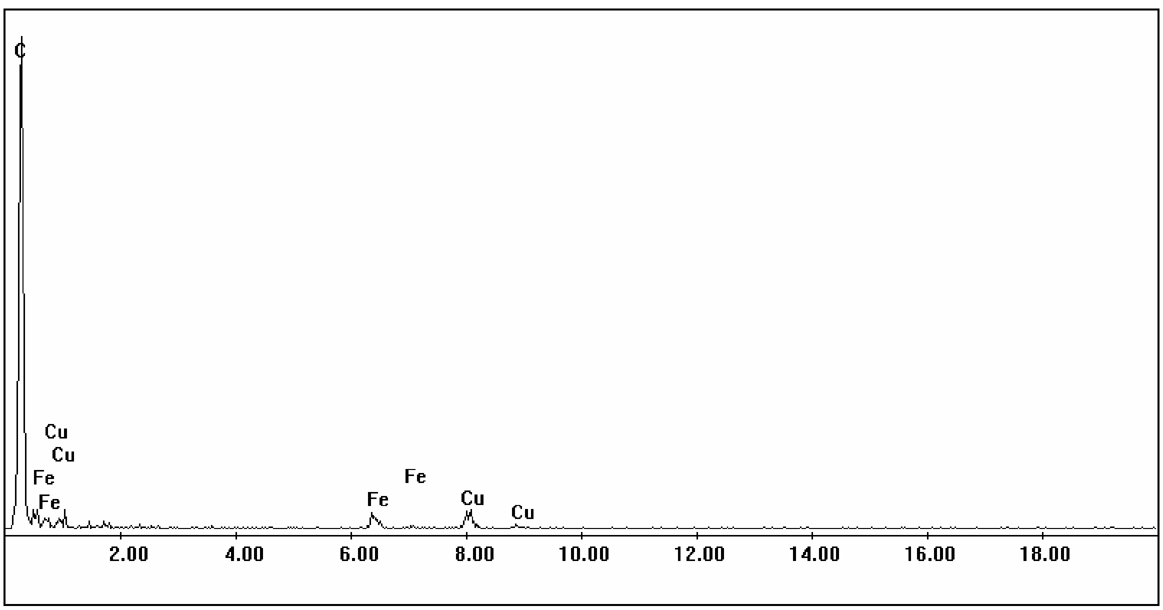

Figure 5. EDS shows the presence of Fe.

Mössbauer spectroscopy of the filled MWCNTs, figure 6, shows the presence of Fe nanoparticles. The signal was weak due to the low number of Mössbauer nuclei; in this case, the nucleus of iron or one of its phases in the sample data was collected over a period of 90 hr, which is a relatively long period. For comparison, the spectrum of pure iron foil used as a standard for calibration is shown in figure 7.

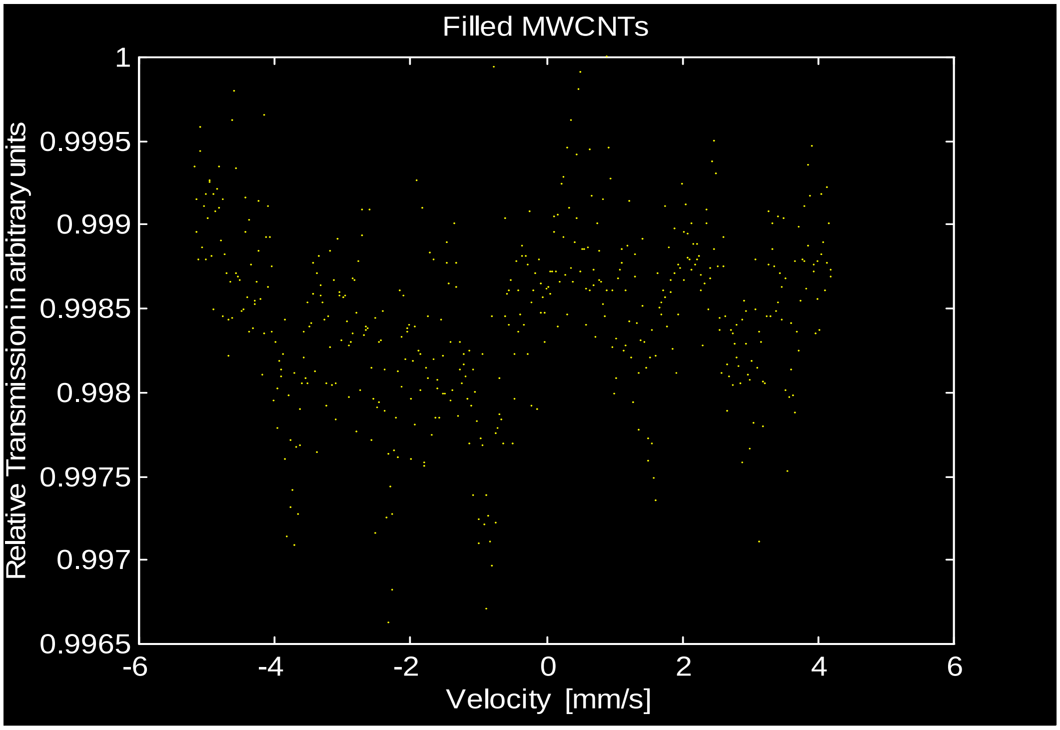

Figure 6. Mössbauer spectrum of filled MWCNTs.

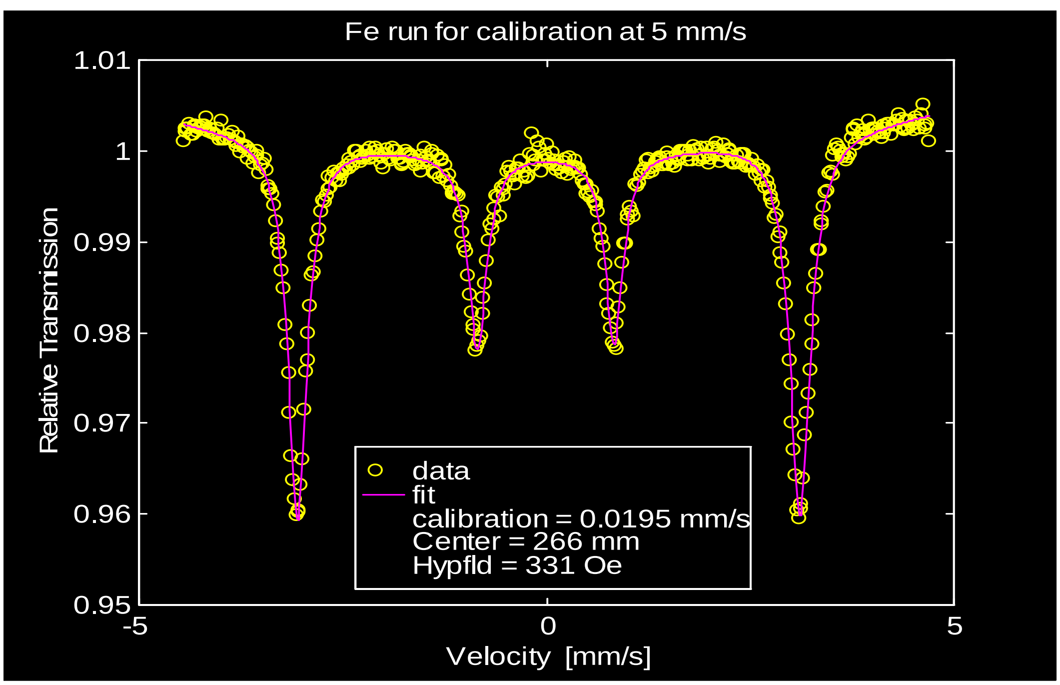

Figure 7. Mössbauer calibration run using Fe foil.

4. Conclusions

Synthesizing exotic materials such as alternate permanent magnetic materials, magneto-resistant materials, and other materials with interesting properties inside of CNTs has several potential applications in NEMSs; it is also interesting for the fundamental study of 1-D properties of solid matter. The synthesis of low-dimensional magnetic particles is important for the investigation of unusual behavior of magnetic quantum size effects. For low-dimensional magnetic particles there is a wide range of technological applications, from memory devices to cancer therapies. To make the preparation of low-dimensional magnetic particles attractive for technological applications, it is favorable to find easy ways of preparation, low cost synthesis procedures, as well as state-of-the-art industrial scale preparation techniques.

The chemical method used in this project has proved to be promising as a base line in synthesizing magnetic materials at the nano scale. More research is required to understand the parameters that control the filling yield and uniformity. It is also desirable to find new methods to fill not only MWCNTs but also CNTs.

The fabrication of nanowires using the CNTs as templates will provide a new approach to nanofabrication. The dynamics of wetting and capillarity might be studied in situ and the high reactivity of the tube caps remains to be understood.

The internal volume of a nanotube can also be used as a test tube for studying chemical reactions, or the thermodynamics or kinetics of phase transitions in small spaces.

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